SHIBAURA INSTITUTE OF TECHNOLOGY

Corrosion Protection of Zinc Rich Paint Coating on Steels

by

Azizul Helmi Bin Sofian

Graduate School of Engineering and Science

March 2014

SHIBAURA INSTITUTE OF TECHNOLOGY

Abstract

Graduate School of Engineering and Science

Doctor of Philosophy

by Azizul Helmi Bin Sofian

Special attention has been paid since late 1950s to the studies aimed at improving and betterment the application of means of corrosion protection of metals as one of the methods for saving natural resources and increasing the durability of machines, building structures and other equipment. In order to protect metals against corrosion, coating is one of the promising method that can be employed. At the same time, insufficient attention has been given to the mechanism aspects of evaluating the efficiency of the protective coating. Recognising that there exist significant shortcomings in currently available information on corrosion mechanism, we are motivated to investigate the anti-corrosive protection by zinc rich paints (ZRP) using the commercial paints in the market. The research work was structured by coating metallic substrate with two diffent kind of ZRP with zinc content of 74 wt.% and 96 wt.%. Based on this coated materials, three main studies; specifically on corrosion performance in corrosive agent, comparison in different concentration of corrosive agents and evaluation on protective coating using electrochemical impedance spectroscopy (EIS).

1. Zinc rich paints (ZRP) are one of the most effective coatings used to protect steel from corrosion and they have been studied under severe environment like seawater, marine and industrial environments. A major problem in classic solvent-based paint is the emission of volatile organic compounds (VOC), which contribute to atmospheric pollution. In this study, the corrosion behavior of an epoxy based ZRP with less organic solvent so they abide by environment standards was studied. In this work, metal substrate was coated with various thicknesses of coatings of ZRP and the cross-section of the coating was observed by means of scanning electron microscopy (SEM), electrochemical behaviors were compared using potential corrosion measurement system and open circuit measurement. It was verified that both coatings with 74 wt.% and 96 wt.% showed good corrosion resistance mainly due to the cathodic protection and barrier effect, respectively. However, for single layer coating of 74 wt.% Zn, does not offer good corrosion protection.Based on

results from morphology characteristics of ZRP at initial stage, a probable current density inhibition model was proposed.

2. The second study deals on the evaluation of coated samples in two different concentration of corrosive agents, 0.5 and 1.0 M NaCl solution. The electrochemical behaviour were investigated based on polarization measurement, open circuit potential and electrochemical impedance spectroscopy (EIS). To confirm our coating is stable in thickness, SEM observation on the cross-section was conducted. The performance of the coating with different coating thickness varied particularly in coating system of 74 wt.%-ZRP. Using Stean-Greary equation, the polarization resistance (R_p) was determined from the Tafel plots and we also calculate the corrosion rate (V_{corr} in millimetre per year) . In 0.5 M NaCl solution, coating system with 96%-5 shows the lowest corrosion rate. Coating systems with 74%-ZRP do performed well, and remarkably sample with 5 layers show the best performance in that system. There was a correlation between zinc content and corrosion resistance performance. Film thickness of the coated samples with 74% probably affected the electrochemical properties and the corrosion resistance performance.

3. The third study evaluates the corrosion performance of the coating systems by using electrochemical impedance spectroscopy (EIS). EIS was used to monitor, up to 7 weeks, the degradation kinetics of three different thickness under cathodic protection in NaCl solution were conducted. EIS in the 100kHz-1mHz frequency range was employed as the main electrochemical technique to study the corrosion behaviour of ZRP. The EIS results obtained at the open circuit corrosion potential have been interpreted using a model associate the impedance of parcel to particle contact to account for increasing resistance between zinc particles with immersion time, in addition to the impedance due to zinc surface oxide layer and the resistivity of the binder. From the results, we conclude that the loss of cathodic protection is due to the decreases of the zinc and metallic substrate area ratio due to zinc corrosion and the loss of electric contact between Zn to Zn particles, and this can be confirmed from SEM observation. Coated sample with 74 wt.%-ZRP shows severe corroded zinc particles, while 96 wt.% sample relatively still maintain the spherical shape of zinc particle. Even when cathodic protection effect by Zn particle became weak, the metallic substrate is still protected against corrosion by the barrier effect and reinforced by zinc corrosion products.

Contents

List of Figures

List of Tables

Abbreviations

EEC	**E**lectrochemical **E**quivalent **C**ircuit
Fe	Iron
$Fe(OH_2)$	Ferum Hydroxide
Fe_2O_3	Ferric Oxide
H_2O	Water
NaCl	Sodium Chloride
O_2	Oxygen
SEM	**S**canning **E**lectron **M**icroscopy
Zn	Zinc
ZRP	**Z**inc **R**ich **P**aint

Symbols

C	absolute capacitance	F
C_{dl}	double layer capacitance	F
I	current	A
Q_{cc}	$s^n\Omega^{-1}$	
Q_f	constant phase element of coating film	Ω
Q_{dl}	constant phase element of double layer	Ω
R_c	resistance of charging circuit	Ω
R_{ct}	charge transfer resistance	Ω
R_f	resistance of coating film	Ω
R_s	resistance of solution or electrolyte	Ω
Y_{dl}	pre-factor of constant phase element Q_{dl}	$s^n\Omega^{-1}$
Z^*	complex electrochemical impedance	Ω
Z'	real part of electrochemical impedance	Ω
Z''	imaginary part of electrochemical impedance	Ω
Z_c	impedance of capacitor C	Ω
Z_q	impedance of constant phase element Q	Ω
Z_r	impedance of resistor R	Ω
ω	angular frequency	$rads^{-1}$

Chapter 1

Introduction

The application [1] of zinc rich paints (ZRP) metal substrates is a very efficient approach of corrosion resistance protection. They are used in many aggressive media such as sea water, marine and industrial environments. Today, thousands of industrial manufacturers depend on paint or coating for long lasting strength, protection and improve productivity. The main area zinc has been depicted to be more effective than other coatings types. Furthermore, the current *Clarke* number of zinc is 0.004% exceptionally very small value and the needs in reducing zinc consumption is very crucial [2]. As the global economy is expanding at a decent pace, manufacturing and construction development in BRICs countries and other major developed countries the usage of steel keep expanding. Therefore, the demands of zinc rich paint, zinc plating application are growing everyday. Compared to electroplating, not only the consumption of zinc can be reduced, power saving and shortening the manufacturing time also can be expected by using the paint. The protection of steel with epoxy based zinc rich paint is based on the general principle of cathodic protection by metallic zinc in contact with metal substrates. It is a common fact that in order to achieve a long life coating system, a zinc primer needs to be applied as the first coat. For solvent based zinc rich paints, it seems to be established that, at least at the beginning of immersion, zinc particles provide [3, 4]. Then, a long term protection develops due to the formation of zinc corrosion products, reinforcing the barrier effect of the paint [5].

The metallic zinc content in the dry film is a very important parameter to be emphasized in the technical specifications of zinc rich paints. However, as observed by Lindquist *et al.* [6] this parameter is not the only factor determining the performance of this kind of paint. For example, Fragata [7] Del Amo [8] and Pereira *et al.*[9] verified that the chemical nature of the binder and the zinc particle size are also very important. The zinc particle (spherical or lamellar shape, or a combination of both shape) is dispersed

in an inorganic (usually orthosilicates) or organic binder (usually epoxies) [10]. These particles must be in electrical contact between themselves and the metallic substrate in order to secure a well established electrical conduction within the coating. In such condition of percolation, a galvanic coupling is created between zinc and the metal substrates which is nobler than zinc. Then, zinc can preferentially dissolve, acting as sacrificial pigment, and allowing a cathodic protection of the metal substrate. Many studies [11, 12, 13, 14, 15, 16, 17, 18, 19] exist in literature and relate the protection mechanisms and degradation processes of such coatings. Physico-chemical properties and corrosion resistance of solvent based zinc rich paints strongly depend on pigment volume concentration (PVC), shape and size of zinc particle [4, 20]. In common liquid ZRP, zinc usually introduced as spherical particles with mean diameter ranging from 5 to 10 μm. To ensure good electrical contacts between zinc pigments and the steel substrates, a high pigment concentration is required (usually above 60 wt.% by volume in solvent based zinc rich paints) [20]. A major drawback of classic solvent based paint is the emission of volatile organic compounds (VOC), which contribute to atmospheric pollution. Since the 1970s, powder coatings are often preferred because they are composed of dry thermosetting powder (without organic solvent) and more environment abiding.

Another type of zinc rich paint was introduced in the middle of 1990s in the automative industry with the intention of imparting weldability to organic coating [21]. The steel sheets were joined partly with each other at some sites during assembly into the automobile body. Since such overlapped areas of steel sheets were difficult to be treated with paint or phosphate solutions, they became highly susceptible to corrosion. As a solution for this problem, cavity wax spray was employed to seal overlapped sites of steel sheets to prevent corrosive factors from approaching the joint sites. However, this method caused low productivity and higher production costs. In consequence, pre-coated steel sheets with paints that allow the welding of coated metal was proposed as an alternative to overcome the problem. Much effort has been invested to improved the corrosion resistance and weldability of the coating incorporating.

1.1 Motivation and Objectives

The main problem with liquid ZRP concerns the emission of volatile organic compounds (VOC) into the atmosphere. That is the reason why powder coatings are often preferred, because they are composed of dry thermosetting powders. However, the zinc content in powder ZRP is usually well below the one reported in liquid ZRP. Indeed, above 70 wt.% of zinc particles , the powder (after extrusion and before application) is not homogeneous which induces problems of zinc dispersion into final coating (after application). In a zinc

rich paint with epoxy based with 90 wt.% zinc, the volume concentration of the zinc will be approximately 60 wt.%, due to the difference in specific gravity. Due to the lower zinc volume concentration usually found in epoxies and the insulating and protecting properties of the epoxy binder. one may ask whether zinc epoxy based coating systems are more susceptible to degradation in corrosive environments. Moreover, percolation and porosity are affected by low zinc content which means that effectiveness and interest of these "zinc rich" coatings can be discussed. The corrosion behaviours of zinc rich paint with various thickness ranging from 10μm to 50μm, in two types of zinc rich paint with zinc contents of 74 wt.% and 96 wt.% was investigated to find out key factors of corrosion mechanism. In addition, the cathodic protection ability of zinc rich coating on metal substrate was evaluated.

1.2 Thesis Outline & Contributions

1.2.1 Chapter 4: Corrosion Performance of ZRPs on mild steel in 0.5 M NaCl solution

The chapter discusses on the preparation of coated samples using commercial ZRPs with different thickness. The corrosion behaviors/performances of zinc rich paint (ZRP) applied on steel substrates under NaCl solution environment were investigated by using electrochemical measurements, scanning electronic microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) and the results are presented in this chapter.

1.2.2 Chapter 5: Comparison of corrosion resistance in different concentration solution

The chapter consists of the electrical properties evaluation of coated samples with ZRP-74 wt.% and 96 wt.% in two different concentration solutions. The influence of the zinc content on the paint behavior has been studied, but little attention has been paid to steel/paint corrosion product, which simulates practical application conditions. In this chapter, we reports an evaluation of the corrosion behaviors/performances of zinc rich paint (ZRP) applied on steel substrates under NaCl solution as artificial seashore environment by using polarization measurements and Electrochemical Impedance Spectroscopy (EIS) in two different corrosive media. Understanding the coating behaviour in severe solution will lead to a new high corrosion protection coating design.

1.2.3 Chapter 6: EIS characterisation of ZRP coating

Characterization of coated ZRP as anti-corrosive coating for metallic substrate using EIS is presented in this chapter. The performance of the materials was investigated practically based on two different types of commercial ZRP, 74 wt.% and 96 wt.% with three different kind of thickness using open circuit potential and electrochemical impedance spectroscopy measurements. Comparison of these samples in different duration of immersion was also carried out and is presented in detail in this chapter. By utilizing EIS measurement, superior performance of ZRP in severe corrosive media could be understood deeply, as we fitted our data using the suggested electrical equivalent circuit.

1.2.4 Chapter 7: Conclusions & future works

The final chapter concludes all the studies that have been conducted and their remark contributions. In addition, extension studies on ZRPs optimum design, mathematical and circuitry analyses are suggested in this chapter.

Chapter 2

Background Theory

In this chapter introductory theory will be elaborate to give the reader a deeper understanding of the basic concepts of zinc rich paints and the application of zinc rich paints in anticorrosive paint systems for the protection of steel. The theory section is divided into 4 sections, each with their own subject area. Section 2.1 will be discussing general aspects of zinc rich paint, section 2.2 describes basic corrosion theory and mechanisms, and 2.3 describes type of corrosion. Sections 2.4 describes the composition and formulation of anti-corrosive paint systems.

2.1 Zinc rich paints

This section will describes the basic chemical and physical characteristic of zinc rich paint with silicate and epoxy based. In particular, the chemical structure and its importance for different physical and chemical properties are presented.

2.1.1 Introduction to zinc rich primer

What is a zinc rich primer and how is it possible to protect bare metal from corrosion?

Zinc rich primer besides being a good barrier to oxygen and water may also protect the metal galvanically. For betterment in corrosion resistance the conductivity of the coating should be high and provide necessary conductivity for galvanic protection. High concentration of zinc, contributes to the film or coating's porosity and its poor internal adherence. The coating of silicate base of ZRP frequently do not bond well to each other and it is better to coat the metallic substrate using an organic zinc-rich paint. Inorganic zinc primers and, to a lesser extent, organic zincs have been effective in moderating

corrosion in extremely aggressive environment such as seashore and marine environment.Their pricing is tied to the current price of zinc in the markets. Paint formulators have used variety of additives to reduce the occurrence of pinholes and cracks. The major problem is air entrained in the metallic substrate during the paint application. Although most of the air escapes from the paint without causing problems, a compelling quantity remains as tiny bubbles until the film is in its final stages of drying process. Therefore, to achieve maximum performance, most researchers attempt to coat the metallic substrate with thin coat, in order to allow the coat to dry fast without occurrence of cracks. In many environments the presence of pinholes in film or coating does not result in excessive corrosion. This surprise is probably due to high surface tension of solution, causing it form droplets rather than flowing on hydrophobic resin surfaces. However, in certain device, for example in tank lining work, pinholes cannot be tolerated [22]

While zinc silicate is a typical "new building" coating, organic zinc rich paint is more of a maintenance primer. The epoxy base primer is far more easy to apply in higher thickness without cracking and can be applied with conventional airless spray, while alkali silicates normally need special equipment. Organic zinc rich coatings are not as electrically conductive as inorganic zinc rich coatings, thus, they have lower level of galvanic protection. We need to remind here that, organic zinc rich paints do not require as high a level of blast cleaned metallic surface as do inorganic coatings and they are easier to handle even for layman [23].

2.2 Corrosion of steel

Corrosion of steel is a well known problem, and can be recognized by the formation of red rust on the surface. In order for steel to corrode and form rust, anodic and cathodic reaction must take place. In the anodic reaction iron is oxidized and forms divalent cation Fe^{2+} with the liberation of two electrons (reaction 2.1). In reality, the most frequent cathodic reaction is the reduction of oxygen, as shown in reaction 2.2

$$Fe \longrightarrow Fe^{2+} + 2e^{-} \tag{2.1}$$

$$O_2 + 2H_2O + 4e^{-} \longrightarrow 4OH^{-} \tag{2.2}$$

The iron ions given in reaction 2.1 will subsequently react with the hydroxide ions and form the complex iron hydroxide:

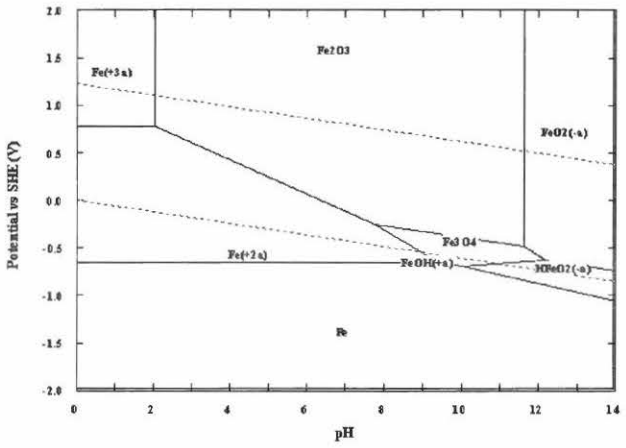

FIGURE 2.1: Pourbaix diagram for iron in water

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \tag{2.3}$$

Since oxygen dissolves readily in water, there is normally an excess of it. A further reaction with the formation of the well known red rust can therefore take place as shown in reaction 2.4

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2Fe_2O_3 \cdot H_2O + 4H_2O \tag{2.4}$$

The stability of iron may be depicted by means of a Porbaix diagram. Figure 2.1 shows the Pourbaix diagram for iron substrate in water at 30°C
with an ion molarity of 1.0×10^{-6}. As depicted on Figure 2.1, iron is only immune at a potential below -0.65V. Above the immune area, iron will corrode in acidic environments with the formation of Fe^{2+} or Fe^{3+}. In neutral environments, iron will have tendency to form oxides normally as Fe_2O_3 or Fe_3O_4. In strongly alkaline environments, iron will corrode and form either FeO_2^- or $HFeO_2^-$.

It is important to state that the presence of chloride ions in the environments has a big influence on the stability of iron metal and increase the risk of active corrosion. the ability of iron to form oxides will additionally decrease and the passive properties are harder to reach.

2.3 Corrosion of coated steel

The protective nature of corrosion resistance paint system is only valid for a given time and the destruction of the paint coating will eventually take place leaving free passage entrance for corrosive agents to penetrate towards metal substrates. normal failure mechanisms related to organic coatings include blistering and under cutting corrosion, which are fatal for the protective behaviour of the coating and chalking or fading, which are less risky. Blister paint are formed when water and other corrosive agents percolate the paint coating during time of wetness. Access of corrosive agents cause a corrosive reaction to take place underneath the coating and cause the paint film to swell, as illustrated in Figure 2.2. As the blister grows, it often be condusive to combine with other blister can be formed according to Table 2.1.

The osmotic blister is most common and is created near contaminants on the metal surface. An osmotic blister is the ordinary and created contaminants vicinity on the metal surface. An osmotic blister is conceived when water percolate the paint and

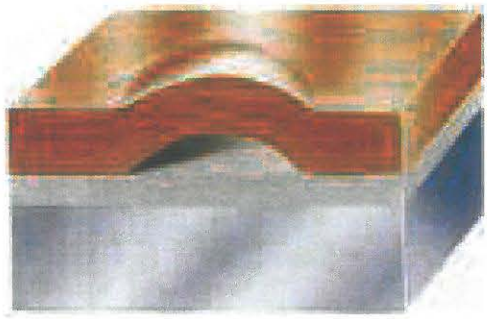

FIGURE 2.2: Schematic of a blister

TABLE 2.1: Types of blister

No	Type of blister
1	Osmotic blister
2	Anodic blister
3	Cathodic blister

dissolves soluble substances in the paint. This produce a dense fluid beneath the paint which is drawn to the solution outside the paint by osmosis. The blister is developed as an attempt to equalize the density between these two fluids. [24]. Undercutting corrosion is developed near scribe or sheared edges as illustrated in Figure 2.3. The corrosion will normally occur either by a chemical reaction in the interface between substrate material and paint, or by corrosion of the substrate metal itself. Both situations will decrease the adhesion, or unfavourable case, completely disconnect the paint film. The mechanism of undercutting corrosion can be described as a crevice corrosion scenario. Crevice corrosion is characterized by the presence of a small local anode and a large external cathode. Formation of an acidic environment and gaseous hydrogen in the crevice will further accelerate the corrosion [25]

Another kind of crevice corrosion is often present on painted aluminium and it is known as filiform corrosion. Filiform corrosion is initiated near defects and mechanical damages in the paint from which fine passageways containing corrosive products are spread in a smeared pattern. The mechanism behind filiform corrosion is directed by an active "head", which acts as an anode, while the "tail" and the surrounding regions act as a cathode. A potential difference of 0.1 to 0.2V is generally obtained between the head and tail region. The presence of oxygen is crucial for the maintenance of cathodic reactions, and therefore the motivation behind the mechanism of filiform corrosion. The cathodic reactions take place in the tail region, which is supplied with oxygen and condensed vapour through cracks and crevices in the coating. The head of the filament is filled with floating flakes of opal aluminium gel which are moving towards the tail region. Reactions between aluminium ions (Al^{3+}) and hydroxide ions (OH^-) will also take place in the tail region, producing aluminium trihydroxide ($Al(OH)_3$) and aluminium

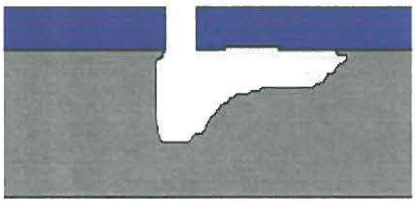

FIGURE 2.3: Schematic diagram of undercutting corrosion

oxide (Al_2O_3). Filiform corrosion is generally dependent on the ratline humidity and the quality of the applied surface treatment. Serious attacks appears in warm coast regions, where high salinity and high relative humidity increases the development of filiform corrosion. Filiform corrosion is only present in the atmosphere and occurs especially at a relative humidity of 85% to 95%. [26]. Cathodic protection of steel by means of sacrificial anodes (eg. zinc) or impressed current can result in cathodic disbondment which decreases the adhesion of the paint coating. The loss of adhesion between the paint and substrate material, is caused by formation of cathodic reaction products (eg. OH^-) near flawed areas in the paint coating. Cathodic protection thus increases the risk of disbandment since cathodic polarised steel surface has a higher exposure to cathodic reactions. A model for the mechanism of cathodic disbandment is illustrated in figure, with the presence of cathodic reaction products beneath the paint coating.

Studies of the mechanism behaviour have shown that production of hydroxyl ions is the primary cause of cathodic disbondment. A direct proportionality is present between the OH^- concentration and the rate of disbandment. It is believed that the generated hydroxyl ions interact with the paint and thus weaken and break the bonds between the paint and the steel substrate. The oxygen concentration in the environment is another factor that enhances the risk of cathodic disbondment [27]

2.4 Anti-corrosive paint

An introduction to general aspects of paint composition and properties is needed in order to understand the mechanism of anti-corrosive paint systems. Paint is a complex formulation based on many different components which contribute to the overall efficiency of the system. This section describes the different components and their mode of operation.

2.4.1 What is paint?

Paint is an organic coating that primarily protects equipment and constructions from environmental damage and provides a decorative surface. For protection purposes, paint is used in a wide range of industrial application such as ships, ballast tanks, drilling rigs and concrete constructions. Selecting the right kind of paint system requires a comprehensive knowledge about the environment and its demands. Protection is a wide area of expertise and requires information about problems related to corrosion, fouling, contaminations, wear and abrasion. Paint as definition, composed of a liquid material which transforms to a thin coherent and adherent film when applied to a surface.

The composition of paint can generally be divided into four main components: binder, pigment, solvent and additive. The binder is the backbone of a paint system and is therefore used to classify the system.

Generally, organic solvent based paint can be divided into two groups: physically drying paint and chemically curing paint. This categorisation concerns the action of film formation and describes whether the transition from liquid to solid state takes place either by evaporation or by chemical reaction.

Physically drying paints form a film exclusively by evaporation of solvents. The binder molecules have therefore the same composition and size both before and after solidification of the film. The mechanism of physically drying paint is physical process where the solvents evaporate and leave behind long chains of resin molecules, which pack together and form a coherent plastic film. Chemically curing paint is based on a curing mechanism where the film formation takes place by a chemical reaction between the binder and a curing agent. The final binder molecules in the dry film are therefore different from the initial binder molecules. The final binder molecules are much bigger and contain a high degree of cross-linking, forming a strong and non-reversible paint film [28].

A description of the four main components is given in the following four sub-sections. Each section describes the most common components, their mechanism and application.

2.4.2 Binders

The binder is an essential component that provides uniformity and coherence to the paint system. It holds the pigments together when a dry film is formed, and provides adhesion to the substrate material. The type of binder often determines the durability of the final product. The ability of a binder to form a dense and tight film is directly related to its molecular weight and complexity. Binders with a high molecular weight often tend to form film by evaporation, while low-molecular binders generally will form film by a reaction in situ. A way to classify a binder is according to its chemical reactions. Table 2.2 lists some important binders, their grouping and chemical reactions.

2.4.3 Pigments

Pigments compose a broad group of dry powder materials which are added to the paint in order to provide functionality and appearance to the paint system. The pigments are insoluble in the paint system and range from naturally occurring minerals to synthetic organic materials. Besides the obvious purpose of providing colour and opacity, pigments

are also an import an additive for corrosion protection, film reinforcement, coverage and adhesion. In anti-corrosive paint systems, pigments mainly provide protection by one or more of the following mechanism; inhibition of corrosion, passivation of substrate metal, barrier against water permeability and cathodic protection. Certain pigments also elevate heat, abrasion, acid or alkali resistance to the final dry film. Important properties for all pigments are particle size and shape, wet ability by the binder and bulking. Some important pigments, their grouping and functionality are listed in Table 2.3.

2.4.4 Solvents

Solvents are volatile liquid substances with the purpose to dissolve solid paint fractions, reduce the viscosity and make the paint fluid for satisfactory appliance. After application, the solvent must evaporate to allow the coating t cure and achieve hardness. If a solvent has low volatility it can cause runs and sags in the drying coating film. In contradiction, solvents can not be too volatile and cause solvent pops, loss of gloss, dry spray, poor surface wetting and penetration, poor film flow and inhibit cure. A blend of different solvents is therefore normally used in order to achieve optimum properties. Solvents are usually categorized according to their chemical composition. Table 2.4 list some important groups of solvents, their advantages and disadvantages.

TABLE 2.2: Classification scheme of binders according to their chemical reactions

Classification	Examples	Chemical reactions
Oxygen reactive binders	Alkyds, epoxy esters, urethane alkyds	The binder molecules react with oxygen and a cross-linking the resin molecules takes place
Lacquers	Polyvinyl chloride polymers, chlorinated rubbers, acrylics	Drying mechanism by solvent evaporation. The long chain resins entangle with each other but no cross-linking exists
Heat conversion binders	Hot melts, Organisols and plastisol, powder coatings	Curing takes place upon heating as the components melt. Both cross-linked and non cross-linked coating are possible
Co-reactive binders	Epoxies, polyurethanes	The film formed by a polymerisation between the resin and curing agent. A three-dimensional network is formed
Inorganic binders	Post-cured silicates, self-curing water silicates, self-curing solvent based silicates	The binders are usually used in zinc particles pigmented primers where a reaction between zinc and binder takes place forming a very hard film
Coalescent binders	Latex	Film formation by coalescence of binder particles dispersed in water

2.4.5 Additives

The final components in a paint system is the additives which normally make less than 1% of the entire paint formulation. Additive are used to balance the paint fluid and modify different physical and chemical properties such as viscosity, surface and interfacial tension, brightness and curing time. Addition of additives is only done when necessary since unwanted consequences on the paint properties are likely to obtain. The most common additives are listed in Table 2.5 with an explanation of their function.

2.5 Corrosion protection by zinc rich paints (ZRP)

The application of zinc metal particles for corrosion protection has been examined for more than 50 years [29]. This section will reviewed different protection mechanisms which are proposed by a number of researchers. According to several studies, zinc rich paints (ZRP) are well known as efficient organic coatings to protect metallic substrates from corrosion. Marchebois *et al.* [30] has reported solvent based ZRP with mixture of zinc pigment varies from 50 or 70wt.%. The zinc concentration was well reported with liquid ZRPs and for the third formulation, conductive pigments (carbon blacks) were added. Then, their electrochemical behaviours wee compared using electrochemical impedance spectroscopy (EIS) and micro-Raman spectroscopy. They found that porosity and electrochemical behaviour was intimately related to the conductive pigments presence in the coating. Two coatings presented behaviours which related to zinc bare

TABLE 2.3: Classification scheme of pigments according to functionality

Classification	Examples	Functionality
Colour pigments	Titanium dioxide, iron oxides, organic azo pigments	Provide colour to the paint. Titanium dioxide is the most popular white pigment because of its high refractive index
Inhibitive pigments	Zinc phosphate, aluminium phosphate, zinc molybdate	Provide active corrosion inhibition to the metal substrate. The pigments are slightly water soluble. Dissolved ion species thus react with the metal to form passivating reaction products
Barrier pigments	Aluminium flake, micaceous iron oxide	Increase the permeation path length to the substrate fro incoming moisture
Hiding pigments	Rutile titanium oxide	Pigments with a high light refractive index to provide good hiding
Extender pigments	Carbonate, silicates, sulphates, barytes and mica	Act as reinforcement and flow control pigments. They are relatively inexpensive